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POLYMERS-SEMICONDUCTORS

-USSR-

by V. Azernikov

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FOREWORD

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Following is the translation of an article by V. Azernikov in Nauka i Zhizn (Science and Life), No 2, Moscow, 1961, pp 8-10.

A Natural Surprise

It would seem that polymers have already given us everything they can; they have revealed their amazing properties to us, which have become a synonym of the name itself. When we hear the word "polymer", our memory automatically brings forth the following epithets: elastic, stable, electro-insulating, and thermally stable. It has become difficult to describe polymers; certainly all of the examples, comparisons, and hyperboles which could be used to help explain them have already been used up. Popularizers are not so much to blame in this as are the polymers themselves...

But nature is more liberal than we think, and often we are confronted with surprises which change our thinking not only about its possibilities, but also about changing the name of entire epochs. In the space of a comparatively short period of time, the 20th century has had several names: "the century of electricity," "the century of radio," "the century of electronics," "the century of atomic energy," "the century of semiconductors," "the century of satellites," and the "century of polymers. But this did not always occur in the form of gifts coming as a pleasant surprise; more often than not, years of unceasing research were required for their discovery.

One of the discoveries in science, which has upset our previous conceptions and which has infringed upon the apparently stable monopoly of inorganic chemistry, has been the existence of semi-conducting properties in organic substances. As is often the case, researchers happened upon this phenomenon long before they had any interest in it. Even half a century ago, it was noticed that the anthracene hydrocarbon had photoconductivity.

But no attention was given to this fact then; a great deal of time and progress in all branches of science was required before this was found to be a regular phenomenon.

Between Two Extremes

Our earth is surrounded by an iron web of conductors. They stretch from pole to pole, they creep into our homes like snakes, carrying heat and light. Conductors are metallic, and metal is a conductor. The walls of a conductor are held up by white rollers. The rollers are made of porcelain, as porcelain is an insulator. These same facts we have learned in school. It took a long time before it could be demonstrated conclusively that substances can be divided into two different classes: conductors and non-conductors, one or the other. But still, it is not quite that simple. Some substances do not fall under one or the other category, but rather halfway in between, partly under one and partly under the other. In addition to that, these substances - which are called semiconductors - occur more frequently than do classic antipodes. Academician A. F. Ioffe has stated that semiconductors almost totally comprise the inorganic world surrounding us.

Their superiority derives from both their quantitative and qualitative predominance. Semiconductors have caused a technological revolution due to their infinite possibilities. They are "capable of" converting alternating current into direct current and of converting thermal energy immediately into electric energy; they can generate radio waves and can increase high-frequency vibrations. And this is only the beginning. It would require an entire chapter to enumerate the possibilities of semiconductors.

This universality, and often simply the irreplaceability of semiconductors, has naturally aroused a great deal of interest in the phenomenon of semi-conductivity. For a long time, it was believed to be connected with the crystalline structure of a solid substance. However, a comparatively short time ago, a Leningrad professor, A. R. Regel¹, discovered these properties in the fusions of solid substances which could not possibly be suspected of crystallinity. But all of these were inorganic substances. And now the last stronghold of the old conceptions has crumbled away - organic semiconductors have appeared.

The electric conductivity of metals is connected with the existence of free valence electrons in them. This is well known. These are carriers of energy in crystalline semiconductors - either electrons or "apertures". This also is well known. And in organic molecules? How is energy transmitted in them?

Stray Electrons

It is a basic fact that the presence of conjugate double bonds in their molecules is a distinguishing feature of organic semiconductors.

The bond can be single, as in saturated compounds, or it can be double, as in unsaturated compounds. If there are single and double bonds in the molecule, this is then a conjugate system.

In each HC = CH group of this unusual "conjugation," there are two so-called electrons. They differ from the others in their

"freedom-loving nature": they do not remain in one place, but can move along the molecule. Naturally, only if the conjugation chain is unbroken, do the double and single bonds rotate in a strict series. The appearance of any group which is disturbing the conjugation in a molecular chain indicates the action of electrons. It is thus clear that an insulator should be inserted in an electric conductor.

Since electrons do not have a strict "visa" and often roam throughout the conjugation chain, it can be stated that they belong not to just one atom, but to all. They are thus called collectivized electrons or delocalized electrons. This delocalization of the electrons is the reason for the "metallic-like quality" of organic molecules and for their electro-physical properties.

The electric conductivity in a conjugation chain is to a great extent connected with its geometry. The simpler is the configuration of a molecule, the fewer fissures will there be in it, and the greater the electric conductivity. In addition, the longer the chain, the greater the number of delocalized electrons, and the easier will be the conductivity. In order that electrons become free, it is necessary that they change from a lower energy level to a higher. If the levels are far from each other, the electron cannot surmount the "abyss" - the energy barrier. Energy outlay is then needed, energy of activation. The closer are the levels, the smaller the amount of energy of activation, and the easier will be the conductivity. When the conjugation chain is short, when there is a small number of electrons, the levels are far from each other. The action of a large number of electrons dissipates the levels; they deteriorate and are changed into wide bands. The greater is the action of the electrons, the wider are the bands, which naturally means a shorter distance between their borders. As the energy "abyss" is narrowed, the conductivity increases.

This is very important. It makes it possible to determine a program of action: in order to form semiconductors of organic materials which can compete with crystalline semiconductors, it is necessary "to construct" a molecule with a huge conjugation chain.

From Molecule to Polymer

Let us imagine the following: you need a jagged, brick wall. How is it going to be made? Obviously, it can be made from the ground up from brick, or it is possible to take a wall which is already built and remove a certain number of bricks at equal distances - in this way the jagged effect is obtained. Although this analogy is not too similar to the task facing the chemist, the choice facing him is the same. It is possible to synthesize macro-molecules with unbroken conjugation -- with poly-conjugation --, or it is possible to take an existing molecule and "make" conjugate double bonds in it. Which method should be used?

A fork in the road of science is confronting the chemist. On the left is a path leading to a macro-molecule with poly-conjugation. On the right is a path leading also to a macro-molecule with poly-conjugation. The choice boils down primarily to the question of which path is easier.

and has been used the most. Secondly, it boils down to the question of which polymer will have the best electro-physical properties.

Up to now we have been speaking about a molecule. But chemists can never be concerned with just single macro-molecules; it is impossible for them to rely upon the operation of chemical conversions. A polymer is involved in the process, and this is not simply the sum of macro-molecules; this is a complex system in which the electric conductivity does not depend on the properties of the macro-molecule alone. In order to pass a current through the polymer, its carriers (electrons or "apertures") must be able to move along the molecules themselves freely and jump from one molecule to another. And this is not so simple, because it depends on the distance between the molecules, on their volumetric amount, and finally on the existence of chemical bonds between them, or in other words bridges, along which the current carriers can pass. Thus, it is still very difficult to make a conversion from molecule to polymer.

This has served to explain the specifics of the work involved, but the experiments themselves often disappear in a cloud of uncertainty, as well as the results, as though they had never even existed. But the end is close in view. The first swallows of the spring of polymer semi-conductor chemistry are rapidly approaching...

What Will the Spring Be Like?

A great deal of imagination is not necessary to envision the possibilities deriving from the use of polymer semiconductors in the different fields of technology. Naturally, these possibilities are not connected just with replacing crystalline semiconductors by polymer semiconductors, although the advantages resulting from this are enormous since polymer semiconductors are cheaper and simpler to produce. There are large amounts of the raw material from which they can be obtained, i.e., natural gas and petroleum. But the main advantage will be derived from the completely new forms of commodities which will be unconventional for the existing semiconductor technology: films, fibers, cloth, compressed powders, etc. And if organic semiconductors can retain the variety and the quality of normal polymers, then the use of semiconductors will have tremendous possibilities as will semiconductor technology.

One can envisage entire "sheets" made of semiconductor cloth, hanging in the sun and converting its energy into electricity. And one can dream of elastic, tubular, chemical reactors, whose walls will act as catalyzers, as well as many other so-called impossible things. And this will not be an unfounded phantasy.

It can be said that this is all still speculation, but even today work is going on which will build a bridge between the present and the future. These studies which were begun several years ago by a group of Soviet scientists, have not only become one of the most promising trends in chemistry, but they have also won worldwide recognition. In the summer of 1960, an International Symposium on Macro-molecular Chemistry was held in Moscow. After it was over, a well-known French chemist,

Sorbonne professor Michel Maga, wrote: "In my opinion, one of the most outstanding studies of recent times is that being done by academicians A. V. Tophiyev, V. A. Kargin, and their co-workers in imparting semiconductor properties to polymers".

Even now it is difficult to predict in what way the work will proceed. Each day, each new experiment can lead to the unexpected, favorable or unfavorable. Naturally one can dream, and it is necessary; work without an aim is a living corpse. And often reality itself turns out to contain the most daring speculations, not in the barrenness of phantasy (do not reproach the scientists or journalists for this), but in the richness and infinite diversity of science.

Instead of referring to the possibilities of using semiconductor polymers, we could instead refer to the fact that it is not difficult to find reasons for doubting their very existence. In all trial work which is in the vanguard, there are difficulties, confusions, and failures. Researchers know this better than any others. But every bit of scientific work must begin somewhere; nothing grows in a vacuum. The most important thing is that a good beginning has been made.